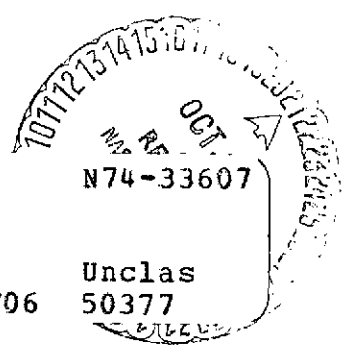
AN INVESTIGATION OF CHANGES IN THE CHEMICAL COMPOSITION OF LOWLAND PEAT IN THE PROCESS OF SELF-HEATING VII. THE FORMATION OF ORGANIC ACIDS

S. S. Mal' and G. I. Maksimenok

Translation of: "Issledovaniye izmeneniy khimicheskogo sostava nizinnogo torfa v protsesse samorazogrevaniya. VII. Obrazovaniye organicheskikh kislot", Vestsi Akademii Navuk Belaruskai SSR, Seryya Khimichnykh Navuk, No. 3, 1971, pp. 87-90



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546 OCTOBER 1974

STANDARD TITLE PAGE

1. Report No. NASA TT F-15,945	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle AN INVESTIGATION OF CHANGES IN THE CHEMICAL COMPOSITION OF LOWLAND PEAT IN THE PROCESS OF SELF-HEATING. VII. THE FORMATION OF ORGANIC ACIDS		5. Report Date October 1974 6. Performing Organization Code
7. Author(s) S. S. Mal' and G. I. Maksimenok		8. Performing Organization Report No. 10. Work Unit No.
9. Performing Organization Name and Address SCITRAN Box 5456 Santa Barbara, CA 93108		11. Contract or Grant No. NASw-2483 13. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		14. Sponsoring Agency Code

15. Supplementary Notes
Translation of "Issledovaniye izmeneniy khimicheskogo sostava nizinnogo torfa v protsesse samorazogrevaniya. VII. Obrazovaniye organicheskikh kislot", Vestsi Akademii Navuk Belaruskai SSR, Seryya Khimichnykh Navuk. No. 3, 1971, pp. 87-90.

16. Abstract Peats with 35-40 and 50% decompn. on storage under conditions favoring biol. activity (<75°) formed small amounts of org. acids (from 0.07-0.11 initially to 0.32-5% in 8 months' storage). On heating at >75°, the acid content rose rapidly to 0.9 - 1.3% in 4 months; the reaction products included glutaric and oxalic acids, their concns. rising with the increasing storage period. At these temps., some hydroxy (glycolic, malic, and lactic) acids were also seen in small amts. The mono-, di-, and hydroxycarboxylic acids identified were typical of the products of oxidative degradation of hydrocarbons. The direct relation noted between the hydrocarbon content of peats and the amts. of org. acids formed on heating them confirmed formation of the acids by chem. conversion of the hydrocarbons.

17. Key Words (Selected by Author(s))	18. Distribution Statement
	Unclassified - Unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	8	

AN INVESTIGATION OF CHANGES IN THE CHEMICAL COMPOSITION OF LOWLAND PEAT IN THE PROCESS OF SELF-HEATING VII. THE FORMATION OF ORGANIC ACIDS*

S. S. Mal' and G. I. Maksimenok

In the process of self-heating of cut peat, a significant increase in the active acidity of the medium is observed, which is usually linked with the accumulation of organic acids. Reports available in the literature on the composition of the acids that form in the process of peat self-heating are few. Bogopol'skiy [1] established the presence of butyric acid bacteria in peat, and established the presence of butyric acid in peat from heating piles. /87**

Strygin [2] cites data on the presence in heating peat of acetic, formic, lactic, and other organic acids whose content strongly increases with an increase in the temperature of heating. At any rate, the investigation of the composition and mechanism of formation of the organic acids has important significance for revealing the character of microbiological processes, and for establishing the chemical transformations that occur during peat self-heating.

---

*Institute of Peat of the Academy of Sciences BSSR.

**Numbers in the margin indicate pagination in the original foreign text.

We showed earlier [3] that in the process of storing block peat with its heating below 75°, the content of organic acids increases slowly, while with an elevation in temperature to above 75°, their amount rapidly increases and reaches 4% of the organic substance of the peat. With the aid of paper chromatography, it was qualitatively established that the newly formed formic and acetic (volatile, with the vapor) acids, as well as oxalic, lactic, glutaric, fumaric, maleic, and citric acids are typical products of the oxidative decomposition of carbohydrates, as is known.

This study posed as its goal a study not only of the qualitative, but also the quantitative composition of the organic acids formed during self-heating.

The investigation was carried out using other types of lowland peat: woody reed (50% degree of decomposition) and woody bog reed (35 - 40% degree of decomposition), stored in test piles at the peat enterprise "Svetlogorskoye". During the period of laying down the test piles, an average sample of peat having a volume of about one cubic meter was taken. Two - three kg peat from the average sample were placed in bags made of porous glass cloth, which were placed by center cross section at depths of 1.0, 2.0, and 4.0 m from the end of the pile. Sampling was carried out 2, 4, and 8 months after the beginning of storage. Observation of temperature in the samples was carried out by means of standard MMT-4a implanted thermistors. The total content of free and bound acids and the individual composition of volatile and nonvolatile acids were measured with the vapor in the selected samples. Extraction of the organic acids from the raw peat was carried out during heating in a water bath over a 4 hour /88 period; the ratio of peat to water was 1 : 25. The content of free acids was determined by direct titration with 0.1 n. solution caustic soda in the presence of phenolphthalein. The acids bound in the form of ammonium salts were titrated after adding formalin which had entered into reaction with ammonia. The volatile acids were measured by means of distillation with the water vapor from the acidified aqueous extract.

TABLE 1. GROUP COMPOSITION OF ORGANIC ACIDS*

Type of peat	Storage time, mos	Depth, m		Maximum heating temperature, °C	Organic acid content calc. for oxalic, % of organic substance of peat			
		At time of stacking	At moment of sampling		Free	Bound	Total	Including volatile & with calc. for acetic
Woody-reed	2	—	—	—	0,047	0,023	0,070	0,026
		4	2,8	51	0,114	0,077	0,191	0,060
		2	1,2	74	0,080	0,134	0,214	0,064
		1	0,6	72	0,074	0,170	0,244	0,018
	4	4	2,3	69	0,057	0,143	0,200	0,041
		2	1,8	79	0,760	0,537	1,297	0,663
		1	0,3	75	0,224	0,276	0,500	0,266
	8	4	1,7	71	0,111	0,207	0,318	0,017
		2	0,7	78	0,594	0,306	0,900	0,454
		1	0,3	75	0,182	0,200	0,382	0,014
Woody-bog reed	2	2	—	—	0,079	0,027	0,106	0,032
		2	1,3	67	0,059	0,154	0,213	0,064
		1	0,7	67	0,124	0,176	0,300	0,053
	4	2	1,0	75	0,312	0,588	0,900	0,068
		1	0,5	70	0,137	0,242	0,379	0,051
		4	1,7	65	0,112	0,236	0,348	0,063
	8	4	1,7	71	0,138	0,209	0,347	0,022
		2	0,7	76	0,754	0,455	1,209	0,057
		1	0,3	70	0,180	0,258	0,438	0,018

* Translator's note: Commas in numbers represent decimal points

Table 1 gives the results of quantitative measurement of the group composition of carbonic acids in the heating peat.

The same table shows the location of sampling bores in the pile, the length of storage time, and the maximum temperature of heating.

In analyzing the numerical material of Table 1, it can be seen that the formation of organic acids mainly depends on the temperature of heating during storage of peat, as well as on the length of storage time. When the temperature of the peat does not exceed 75°, the acid content slowly increases from 0.07 - 0.11 to 0.32 - 0.35%

over 8 months of storage. At a temperature of 75° and above, the amount of organic acids rapidly increases, and in 4 months reaches 0.90 - 1.30° of the organic substance of the peat. At these temperatures, acids also form that are volatile with the vapor, and the amount of such acids reaches 30% of the total amount of acids.

The individual composition of volatile and nonvolatile acids was investigated by the paper chromatography method. For extracting the acids, the aqueous solution was neutralized with a 0.1 n. solution caustic barium to pH 7, boiled dry, and following acidification with 1 ml 6% sulfuric acid, it was processed with grey ether. The /89
acids not vapor volatile were separated in the system of solvents: grey ether-formic acid-water in a ratio by volume of 18 : 9 : 5 [5]; the volatile acids were chromatographed in the following system of solvents: n-butanol-ammonia-ethanol-water in a ratio by volume of 4 : 1 : 1 : 4 [6]. The chromatograms were developed with a 0.4% solution bromcreasol green. The acid spots were cut out, diluted with boiling water three times, and the aliquot part was titrated with a 0.02 n. solution caustic soda in the presence of phenolphthalein. Among the vapor-volatile acids, one spot was found that corresponded to the total of formic and acetic acids. The individual content of acids not volatile with the vapor is shown in Table 2.

Acids with 4 atoms of carbon first appear during the heating of peat: unsaturated (fumaric and maleic) and saturated (succinic), as well as the oxiacids (lactic). As is known, maleic, fumaric, and succinic acids are the products of oxidation of furunol by hydrogen peroxide in the presence of carbonic acids [4]. The latter is formed from the pentoses, which most actively participate in the chemical reactions that occur during self-heating [3].

In the case of intensively heating peat at a temperature of 75° or higher, the amount of saturated dicarbonic acids increases, and glutaric as well as oxalic appear; their amount increases with the increase in length of storage time. At these temperatures, oxiacids are also present in small amounts — glycolic, malic, and lactic.

TABLE 2. INDIVIDUAL COMPOSITION OF ACIDS NOT VAPOR-VOLATILE*

Type of peat	Storage time, mos	Depth, m: During stacking	Depth, m: During sampling	Maximum heating temperature, °C	Acid content, % organic substance of peat: Fumaric	Maleic	Succinic + lactic	Glutaric	Oxalic	Glycolic	Citric	Malic
Woody reed	—	—	—	—	Tr.**	Tr.	Tr.	Tr.	Tr.	—	—	—
	4	4	2,3	75	0,057	0,069	0,055	Tr.	Tr.	—	—	—
	4	1	0,3	75	0,067	0,057	0,067	0,072	0,063	Tr.	—	—
		2	0,8	79	0,089	0,046	0,093	0,064	0,199	0,030	Tr.	Tr.
	8	2	0,7	78	0,090	0,120	0,137	Tr.	0,270	Tr.	Tr.	Tr.
Woody bog reed	—	—	—	—	Tr.	Tr.	Tr.	Tr.	Tr.	—	—	—
	4	2	1,0	75	0,070	0,167	0,116	0,093	0,264	Tr.	Tr.	Tr.
	8	2	0,7	76	0,039	0,079	0,085	0,056	0,286	Tr.	Tr.	Tr.

* Translator's note: Commas in numbers represent decimal points.

** Tr — traces.

All the identified acids are typical products of the oxidative decomposition of carbohydrates. A direct relationship is observed between the content of carbohydrates in the initial peat and the amount of organic acids that form during heating. Thus, during heating of bog peat with a total 17.3% monosaccharides content, the yield of organic acids was 4.1% of the organic substance [3]. During heat, in our case of woody-reed (total monosaccharides 7.1%) and woody-bog peat (total monosaccharides 8.7%), the yield of organic acids fell to 1.2 - 1.3% [7].

Conclusions

1. During the storage of woody-reed and woody-bog peat, as well as in the case of storing bog peat, the formation of organic acids occurs slowly in the region of microbiological activity and /90

with a subsequent increase in temperature. In the case of intensively heating peat at a temperature of 75° and above, the amount of organic acids sharply increases as the result of the ongoing chemical reactions.

2. The monocarbonic, dicarbonic, and oxicarbonic acids of the aliphatic series identified are the typical products of oxidative decomposition of carbohydrates. The direct relationship between the content of carbohydrates in the initial peat and the amount of organic acids in the heating peat confirms the conclusion of the formation of the latter as the result of chemical conversions of the carbohydrates.

References

1. Bogopol'skiy, M. D. In-ta Torfa, No. 13, ONTI NKTP, Moscow-Leningrad, 1934, p. 114.

2. Strygin, N. N. Tr. VNIITP, No. 16, Moscow-Leningrad, 1958, p. 172.

3. Mal', S. S., S. S. Povarkova, N. S. Prikratov, Z. M. Slivka and G. M. Maksimenok. Khimiya tverdogo toplivo, No. 6, 1968, p. 111.

4. Salchinkin, A. P. and R. A. Larina. ZhIKh, Vol. 42, No. 1, 1969, p. 147.

5. Soldatenkov, S. V. and T. A. Mazurov. Metodika kolichestvennoy bumazhnoy khromatografii sakharov, organicheskikh kislot i amino kislot u rasteniy (A Method of Paper Chromatography of the Sugars, Organic Acids and Amino Acids in Plants). Moscow-Leningrad, 1962, p. 35

6. Kuvayev, G. N. and N. S. Imenitov. ZhAKh, Vol. 21, No. 6, 1966, p. 221

7. Povarkova, S. S. and S. S. Mal'. Vestsi AN BSSR, ser. khim. navuk., No. 1, 1971.

Translated for National Aeronautics and Space Administration under contract NASw 2483, by SCITRAN, P. O. BOX 5456, Santa Barbara, California, 93108